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Extensive use of a number of transition metals have been found to isomerize olefinic systems. Two major mechanisms have been proposed to explain olefin reorganization involving transition metal catalysts. One of these mechanisms is the metal hydride addition-elimination mechanism, and the other is the formation of a π-allyl metal hydride complex.

Special attention is given to iron carbonyl catalysts and evidence is presented to support the π-allyl metal hydride mechanism, as well as evidence which appears to draw this particular mechanism into question.

The π-allyl hydridoiron tricarbonyl mechanism, usually accepted as the correct mechanism, requires initial formation of a monoolefiniron tetracarbonyl complex. Upon loss of carbon monoxide from the complex, the coordinatively unsaturated iron tricarbonyl species extracts a hydrogen atom from the host molecule for stabilization to yield the π-allyl hydridoiron tricarbonyl complex. However, investigators were able to isolate the monoolefiniron tetracarbonyl complex by photochemical irradiation of 1,5-cyclooctadiene in the presence of $Fe(CO)_5$, and showed that its thermal activity was contrary to that required by the π-allyl hydridoiron tricarbonyl mechanism. Heating the 1,5-cyclooctadieneiron tetracarbonyl complex produced the 1,5-cyclooctadiene bis(iron tetracarbonyl) complex, and unrearranged 1,5-cyclooctadiene, and no 1,3-cyclooctadiene or the corresponding complex was detected.

Our own results also argue strongly against the π-allyl hydridoiron tricarbonyl mechanism. The monoolefiniron tetracarbonyl complex,

9,9-dichlorobicyclo[6.1.0]non-3-eneiron tetracarbonyl was isolated by photochemical irradiation of 9,9-dichlorobicyclo[6.1.0]non-4-ene in the presence of $Fe(CO)_5$. When 9,9-dichlorobicyclo[6.1.0]non-2-ene was treated in a similar fashion with $Fe(CO)_5$ and ultraviolet irradiation, 9,9-dichlorobicyclo[6.1.0]non-2-eneiron tetracarbonyl was isolated. Futhermore, the 2-eneiron tetracarbonyl complex was rearranged to the 3-eneiron tetracarbonyl complex. This rearrangement occurred with the $Fe(CO)_4$ group intact. From these results, an alternative mechanistic possibility was proposed <u>via</u> a cationic mechanism, i.e. an aluminum chloride catalyzed rearrangement. Instead of forming a complex with an olefin, $Fe(CO)_4$ abstracts a hydride ion from the starting olefin to produce an ion pair, $H\overset{\ominus}{F}e(CO)_4$-cation.

The evidence accumulated and presented in this thesis gives substantial support which argues against the operation of a π-allyl hydridoiron tricarbonyl mechanism, while making the possibility of the $H\overset{\ominus}{F}e(CO)_4$-cation mechanism more feasible.

IRON CARBONYL CATALYZED REARRANGEMENT OF BICYCLO[6.1.0]NONENE SYSTEMS

by

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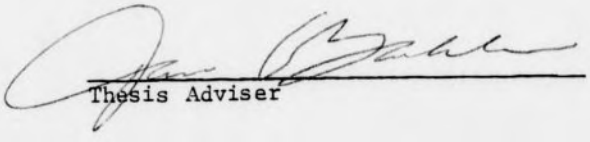

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APPROVAL PAGE

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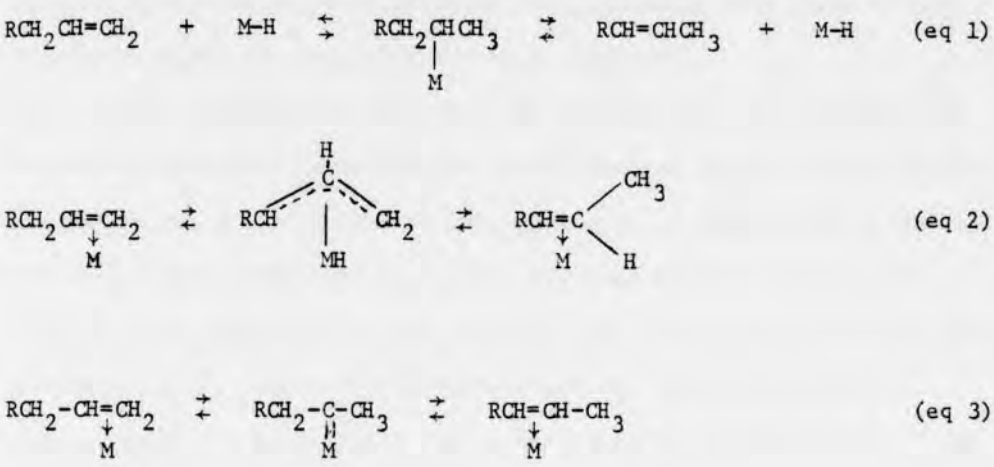
INTRODUCTION

A number of transition metals have been used extensively in effecting the isomerization of olefinic systems, and form one of the very important groups of reagents for this purpose.[1] Some of the most common transition metals employed in these processes, usually used in the form of their organic complexes, are rhodium (I and III), platinum (II), nickel, iron, cobalt, ruthenium, and osmium. It is the purpose of this thesis to review the literature in this area of chemical investigation, and to report the results of our own work regarding the mechanism of those processes catalyzed by iron carbonyls.

Two major mechanisms have been proposed to explain olefin reorganization involving transition metal catalysts. Evidence has been accumulated to support both mechanisms, which appear to depend strongly on the metal used. One of these mechanisms involves addition of a metal hydride to an olefinic system with subsequent elimination of the metal hydride and production of a new olefin (the metal hydride addition-elimination mechanism)[1,2] (eq 1), and the other is the formation of a π-allyl metal hydride complex[1,2] (eq 2). A third mechanistic possibility, for which little evidence exists, requires intermediate formation of a metal-carbene complex[1,2] (eq 3). Finally, a fourth mechanism proposed in more recent work[27] will be discussed later.

For isomerization to occur <u>via</u> the metal hydride addition-elimination mechanism (eq 1), a cocatalyst such as hydrogen or an acid is often necessary, presumably because the cocatalyst reacts with the metal complex



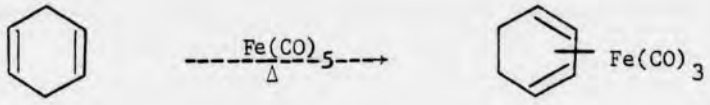
to produce an intermediate metal hydride. Some representative catalyst systems that isomerize olefins via this mechanism are $HCo(CO)_4$,[3] $[(C_2H_4)_2RhCl]_2$,[4] and $Ni[P(OEt)_3]_4$,[4] all of which require an acid as a cocatalyst, and $(Ph_3P)_2PtCl(SnCl_3)$ in the presence of hydrogen.[5]

Representative catalyst systems which isomerize olefins via the π-allyl metal hydride mechanism shown in equation 2 are $Ru_3(CO)_{12}$,[6] $Os_3(CO)_{12}$,[6] and the various iron carbonyls [$Fe(CO)_5$, $Fe_2(CO)_9$, and $Fe_3(CO)_{12}$]. In the following discourse, we will draw special attention to the iron carbonyl catalysts, and present evidence to support the mechanism of equation 2, as well as evidence which appears to draw this particular mechanism into question.

The reaction conditions of the iron carbonyl catalysts have involved thermally as well as photochemically induced rearrangements. Because a discussion of the entire area of transition metal induced rearrangements is beyond the scope of this thesis, and because our own results were

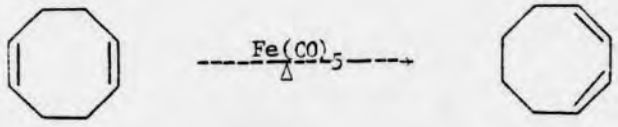
obtained with iron carbonyl reagents, the following discussion will be limited to reactions involving the iron complexes.

The great majority of reactions in which iron carbonyls have been used to effect olefin isomerization have involved direct contact between the olefin and one of the three iron carbonyls.[7] In most cases, interaction results in the formation of a different product olefin. For example, 1,4-cyclohexadiene (1) in the presence of $Fe(CO)_5$ produces the iron tricarbonyl complex of 1,3-cyclohexadiene (2), the result of rearrangement of the original olefin and subsequent complexation of the conjugated diene.[8]



1 2

1,5-Cyclooctadiene (3) when heated with $Fe(CO)_5$ rearranges quantitatively to 1,3-cyclooctadiene (4).[8] In this case however, a dieneiron tricarbonyl complex is not formed, presumably because of its thermal instability due to the strain incurred in the required planar configuration of the diene moiety in the iron tricarbonyl complex.



3 4

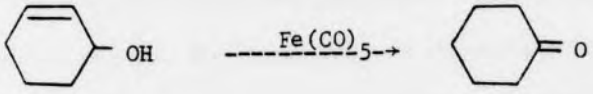
Iron carbonyls can also react with monoolefins to cause extensive isomerization of the double bond. Asinger and Berg showed that 1-dodecene, when heated with $Fe(CO)_5$, produced a mixture of internal olefins.[9] Another example of such a reaction is seen in the isomerization of allyl alcohol (5) to propionaldehyde (7), presumably via the vinyl alcohol (6).[10]

$$CH_2{=}CH{-}CH_2OH \xrightarrow[\Delta]{Fe(CO)_5} (CH_3{-}CH{=}CH{-}OH) \longrightarrow CH_3{-}CH_2{-}\overset{O}{\overset{\|}{C}}H$$

5 6 7

Similar results were obtained from reacting some alkene and cycloalkene alcohols with $Fe(CO)_5$ to yield saturated ketones and aldehydes (eq 4-6).[11]

$$CH_2{=}CHCH_2CH(OH)C_3H_7 \xrightarrow{Fe(CO)_5} C_3H_7\overset{O}{\overset{\|}{C}}C_3H_7 \qquad \text{(eq 4)}$$

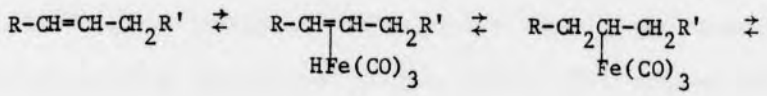


(eq 5)

$$\underline{cis}\text{-}HOCH_2CH_2CH{=}CHC_2H_5 \xrightarrow{Fe(CO)_5} C_5H_{11}\overset{O}{\overset{\|}{C}}H \qquad \text{(eq 6)}$$

There are at least three major advantages of using $Fe(CO)_5$ as an unsaturated alcohol isomerization catalyst in preference to the more conventional acid and base catalysts. Iron pentacarbonyl may be used in low concentrations (3-5%) to cause rapid movement of double bonds within a molecule. An olefin isomerization study of several different strong base and acid catalysts compared to $Fe(CO)_5$ is faster and more complete isomerization catalyst than any of those studied.[12] Secondly, the conditions employed with $Fe(CO)_5$ are mild and have not led to structural rearrangement or polymerization that is characteristic of acid catalysts.[12] Finally, $Fe(CO)_5$ is a relatively neutral material which does not react with a variety of functional groups, such as carboxylic esters, alcohols, and ketones.[11]

It has been shown in a detailed study by Manuel and coworkers that monoolefins are isomerized to give the distribution of isomers which would be expected on the basis of their relative thermodynamic stabilities, that is, the direction of equilibrium achieved during these reactions is toward the more highly substituted olefin, and where geometric isomerism is possible, the trans-isomer predominates. On the basis of these and other data, Manuel proposed two possible rearrangement mechanisms, one a hydridoiron addition-elimination and the other a π-allyl complex mechanism, for the isomerization of monoolefins with $Fe(CO)_5$.[13,14] These two are represented in equations 7 and 8, respectively.



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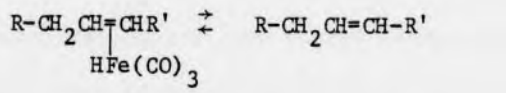
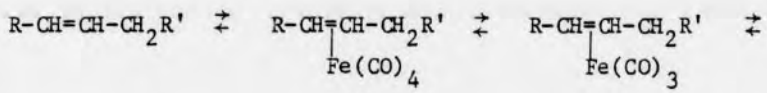


10 (eq 7)



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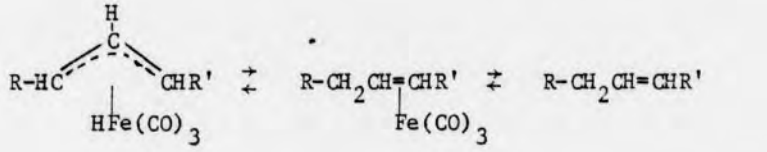


13 (eq 8)

In equation 7, the $HFe(CO)_3$ species would be generated in some manner from $Fe(CO)_5$ and a hydrogen source such as an olefin. Initially, it forms a π-complex with the olefin (8) and subsequently adds homolytically to the double bond to yield the σ-complex (9). This can give rise to a new π-complex (10), which eventually decomposes to produce the new olefin.

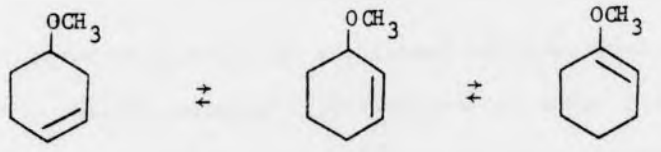
In equation 8, $Fe(CO)_4$ would be generated either thermally or photochemically from $Fe(CO)_5$. The tetracarbonyl species, being highly reactive, complexes with the olefin to form a monoolefin tetracarbonyl

complex (11). Carbon monooxide is lost from 11 to produce the unstable coordinatively unsaturated complex (12). This complex gains stability by extraction of hydrogen from an allylic position to produce the π-allyl complex (13), which ultimately gives rise to products.

Several unsaturated esters and ethers were isomerized with $Fe(CO)_5$. Equilibria of the type shown in equations 9 and 10 were studied. Iron pentacarbonyl in hydrocarbon solvents at reflux or with ultraviolet light was used to catalyze isomerization. Distribution of the double bond to all possible positions was found with this catalyst system.[15]

$$C_5H_{11}CH{=}CHC(=O)CH_3 \rightleftarrows C_4H_9CH{=}CHCH_2C(=O)CH_3 \rightleftarrows C_3H_7CH{=}CHCH_2CH_2C(=O)CH_3 \rightleftarrows$$

5-, 6-, 7-octenoates (eq 9)



4-isomer 3-isomer 1-isomer (eq 10)

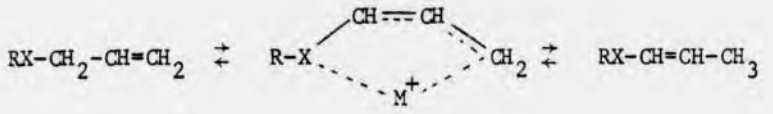
The equilibrium values for the isomers of equation 9 were 18% 2-, 7% 3-, 21% 4-, 24% 5-, 29% 6-, and 1% 7-octenoates (see Figure 1). The values for equation 10 were 95% 1-, 2% 3-, and 3% 4-cyclohexenyl ethers. These data from equations 9 and 10 were rationalized on the basis of two main effects: a) the inductive electron-withdrawal destabilization effects of the carbomethoxy and methoxy groups on olefinic systems, and b) the conjugative destabilization effects of these groups. A carbomethoxy group influenced the stability of an α,β-isomer by opposing conjugative stabilization and inductive destabilization; the net effect of the $-COOCH_3$ unit on the stability of a double bond, as in equation 9, was comparable to the inductive stabilization of an alkyl group.[15] A $-CH_2COOCH_3$ group inductively destabilized an olefin isomer by a factor of ~3 compared to an alkyl group. Thus the 4-, 5-, and 6-isomers are each more stable than the β,γ-isomer (3-) (Figure 1) assuming that the destabilization effect is transmitted through one methylene unit to the β,γ-isomer.[15] A methoxy

	% positional isomer					
$CH_2{=}CHCH_2CH_2CH_2CH_2CH_2CO_2CH_3$:	2	3	4	5	6	7
	17.8	7.3	20.8	24.2	28.7	1.2

Figure 1

group shown in equation 10 stabilized the α,β-isomer by a factor of 10, while a $-CH_2OCH_3$ group destabilized a β,γ-isomer by ~1.5:1 compared to an alkyl group.[15] It was believed that the iron carbonyl reagent was solely a ctatlyst for isomerization and was not involved in the formation of stable olefin-iron carbonyl complexes.[15]

The light induced isomerization of allylic ethers in the presence of $Fe(CO)_5$ has been compared with that brought about by a basic heterogeneous catalyst, KNH_2-Al_2O_3, which isomerizes olefins extremely rapidly and cleanly.[16] The reaction on the basic catalyst is believed to proceed through a mechanism in which the transition state is cyclic, hence directing the reaction in such a way that cis-olefinic products result. Compounds (15) have predominantly cis-configurations during the rearrangements of various olefins [e.g., X = CH_2, O, NR', or $(CH_2)_n$]. The mechanism

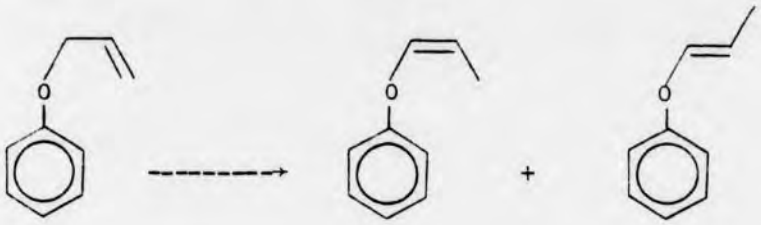


(eq 11)

14 15

of the reaction has been explained in two different ways, first[17] in terms of the greater stability of an allylic carbanion in the cis- rather than in the trans-conformation due to electrostatic interactions of the terminal methyl group with the metal atom, and second by supposing that the cation of the basic catalyst stabilizes the cis-allylic carbanion by formation of a complex (14) through electrostatic interactions. The latter mechanism is more plausible when X is a heteroatom having a lone pair of electrons able to interact with the positve charge of the cation.[18] Hence, the cis-isomer is formed in preference to the trans-isomer.

In contrast, the reaction of phenyl allyl ether (16) with iron pentacarbonyl produced a mixture of the cis- and trans-isomers 17 and 18,



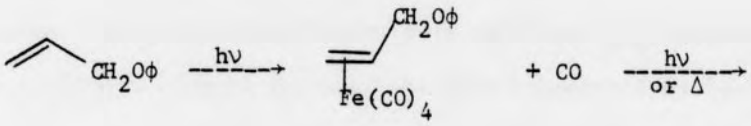
(eq 12)

16 17 18

ratio 17:18 at equilibrium 2:1

respectively (eq 12).[19] A π-complex was reported to be detected by NMR spectroscopy as an intermediate in the reaction but attempts to isolate the complex failed.[19] The formation of a catalyst, presumably $Fe(CO)_4$, which was particularly active for the thermal isomerization of olefinic double bonds was detected during the irradiation of iron pentacarbonyl in allyl phenyl ether.[19] On these bases, the mechanism shown below was proposed for this reaction. This mechanism is of the π-allyl complex type, and is identical in form to that given by equations 2 and 8.

The trans-selectivity in products was greater than predicted. This was explained by suggesting that the oxygen lone pairs may perform the same role as an uncoordinated π-bond in a diene, such as 1,3-pentadiene. However, it was not clear to what extent an analogy could be drawn between an unsaturated ether and a diene. trans-Selectivity in the thermal reaction must be due to a different mechanism. The π-allyl complex (20)



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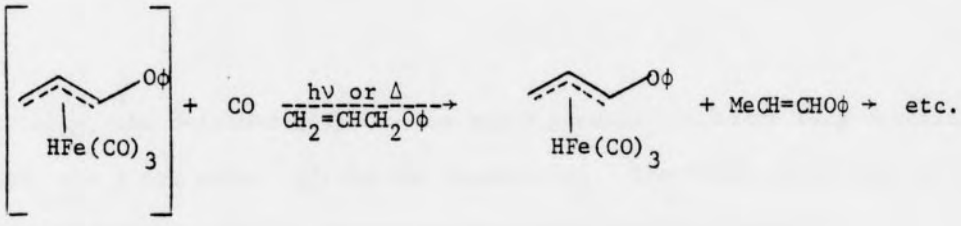
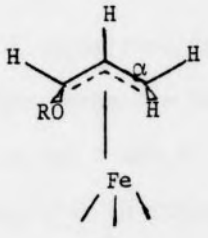
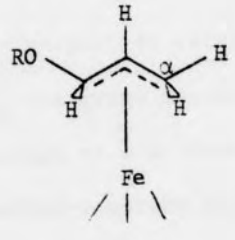


20

may be in either a syn- or an anti-configuration; the syn-, which leads to the trans-product is more stable owing to the decrease in 1,3-interactions between the α-hydrogen and the alkoxy group.[19]

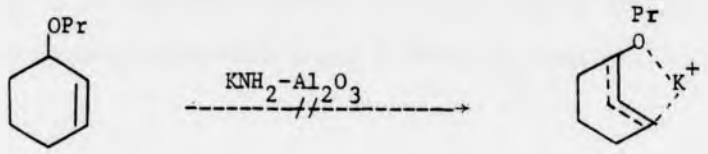


anti-

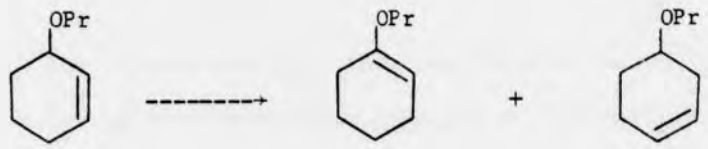


syn-

3-Cyclohexenyl propyl ether (21) was readily isomerized under irradiation with iron pentacarbonyl, whereas it remained unchanged in the presence of very strong bases, such as KNH_2-Al_2O_3, presumably because it could not form an anion of the cis-mechanism type (c.f. eq 11).



Initially, the 4-isomer (23) was the major product but after long reaction times, the vinyl ether (22) became predominate. The vinyl ether (22) is the thermodynamic product because of the stabilization induced by conjugation of the oxygen lone-pair with the double bond.[19]



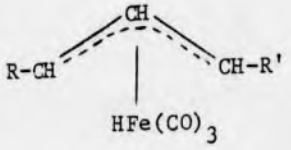
21 22 23

The following results presented here purport to establish a π-allyl metal hydride mechanism for the $Fe_3(CO)_{12}$ catalyzed isomerization of alkenes (c.f. eq 2 and 8). The isomerization of a mixture of 3-ethyl-1-pentene-3-d_1 (24) in the presence of 3-methyl-1-butene (25) resulted in rearrangement products 26 and 27 in which deuterium remained exclusively

in the ethylpentene skeleton (26), demonstrating that deuterium crossover had not occurred.[20] These results suggest that the rearrangement occurs by intramolecular hydrogen transfer. Since deuterium was found only in the three terminal methyl groups of 3-methyl-2-pentene (26) obtained from isomerization of 24, the isomerization was apparently accomplished exclusively by 1,3-hydrogen shifts. A π-allyl metal hydride mechanism appears to be consistent with these observed intramolecular 1,3-hydrogen shifts.

24 25 26 27

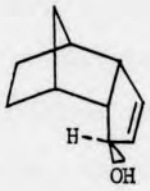
All of the results presented thus far, in fact, are compatable with a mechanism for rearrangement which involves an intermediary π-allyl hydridoiron tricarbonyl complex (28). However, the data are also consistent



28

with a mechanism of hydrogen migration in which hydrogen is transferred suprafacially without the direct formation of an iron-hydrogen bond, that is, a mechanism not requiring the intermediacy of the hydridoiron tricarbonyl complex (28). A suprafacial process is one in which bonds made or broken lie on the same face as the system undergoing reaction.[21]

Cowherd and von Rosenberg proposed a way to distinguish between the two mechanisms, by use of the stereoisomeric alcohols 29 and 30.



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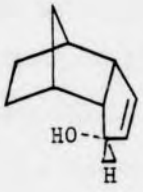

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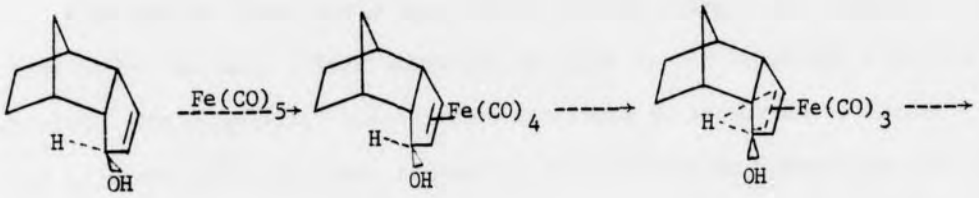
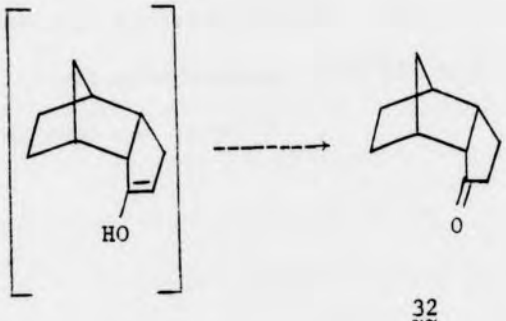


29 31

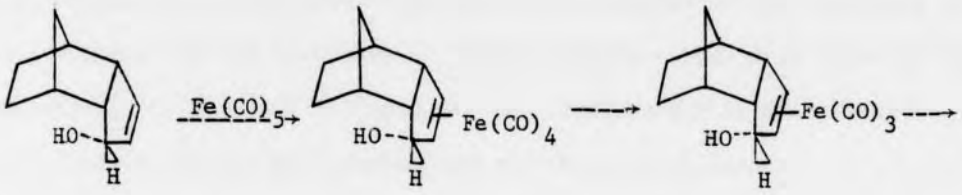


32

(eq 13)

In reference to equation 13, rearrangement of 29 to 32 through a transitional species 31 would be expected to occur if a 1,3-suprafacial hydrogen shift, not involving iron-hydrogen bonds, is operative. In this case, the migrating hydrogen is clearly not properly positioned to allow the formation of a π-allyl hydridoiron tricarbonyl complex because the hydrogen is in the endo-position and the $Fe(CO)_5$ approaches from the exo-side. However, a concerted suprafacial 1,3-hydrogen shift would be expected to proceed without any obvious restraints. In both equations, only approach of $Fe(CO)_5$ from the least hindered exo-side is reasonable. Equation 14 illustrates the isomerization of 30 proceeding to 32 via a π-allyl hydridoiron tricarbonyl complex (33). In 30, the migrating hydrogen is in a favorable position to allow its facile transfer to the iron, and for any rearrangement to occur some mechanism involving iron-hydrogen bonding appears to be reasonable.

A mechanism involving a π-allyl hydridoiron tricarbonyl complex seems to be the most likely mechanism in light of von Rosenberg's actual results. The endo-allyl alcohol (30) was found to isomerize to ketone (32) in about 40% yield when heated at 130° for sixteen hours with ten mole per cent $Fe(CO)_5$ under a nitrogen atmosphere. However, under the same conditions and with prolonged heating at 160°, the exo-allyl alcohol (29) exhibited no detectable change. These results give evidence that a concerted, sigmatropic hydrogen shift of order [1,3] involving no hydrogen-iron bonding does not occur.[22]



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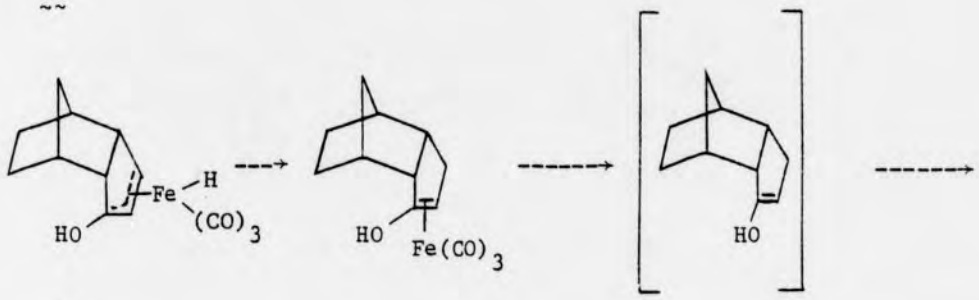

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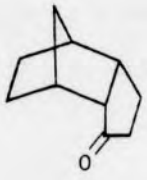


32

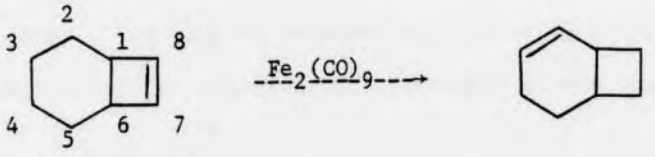
(eq 14)

On heating the deuterio-alcohol (34) with $Fe(CO)_5$ in the presence of cyclohex-2-en-1-ol, only the deuterio-ketone (35) and unlabelled cyclohexanone were obtained showing that crossover of the deuterium had not occurred.[24] This result is similar to the results obtained by Casey and Cyr[20] using purely hydrocarbon systems. The deuterium in the product was found to be in an exo-configuration (34) and migrated with an overall

intramolecular [1,3] suprafacial shift of deuterium on the same side of the molecule as the iron atom.[24] These results, along with those of von Rosenberg,[22,23] appear to implicate the intermediacy of the π-allyl hydridoiron tricarbonyl complex (33) in the rearrangement.

34 35

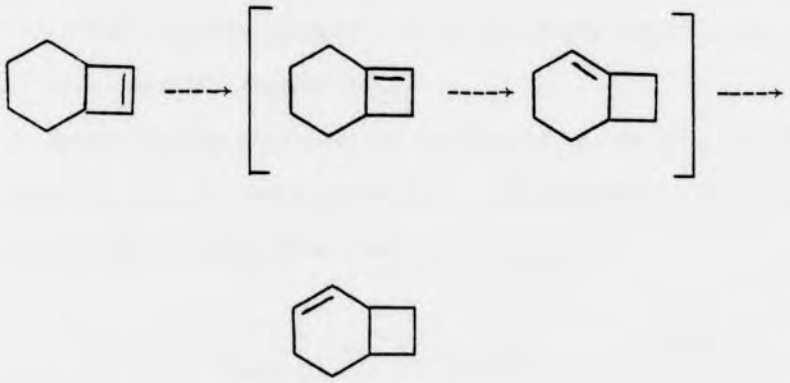
Another example of hydrogen shift is illustrated when bicyclo[4.2.0] oct-7-ene (36) rearranges to bicyclo[4.2.0]oct-2-ene (37) in high yield on treatment with $Fe_2(CO)_9$ in refluxing hexane.[25]



36 37

While other possibilities exist, the rearrangement apparently involves hydrogen transfer from the six-membered ring to the cyclobutene via the iron center without involving opening of the four-membered ring.

There are various mechanistic pathways which can be followed in this reaction. One possibility, the simplest and most likely, involves a series of 1,3-hydrogen shifts which require the intermediacy of the hydrocarbons shown in equation 15.



(eq 15)

Schroeder and Wrighton proposed that a very labile $Fe(CO)_3(alkene)_2$ complex (38) is actually the species responsible for alkene isomerization.[26] Evidence of only monoolefiniron tetracarbonyl (39) was found by infrared spectroscopy. The lack of observable products 38 is likely due to the expected facility of equation 16. No simple alkene complexes of the

$$Fe(CO)_3(alkene)_2 \underset{\leftarrow\!\!-\!\!-\!\!-}{\overset{CO}{-\!\!-\!\!-\!\!-\!\!\rightarrow}} Fe(CO)_4alkene + alkene \qquad \text{(eq 16)}$$

38 39

stoichiometry exhibited by structure 38 have been reported, but $Fe(CO)_3$(methylacrylate)$_2$ has been isolated at low temperatures and decomposes above $-5^{\circ}C$[27] presumably initiated by dissociative loss of an olefin.

Wrighton's suggested mechanism appears in figure 2. Key to the mechanism is the generation of a coordinatively unsaturated metal carbonyl-alkene complex, resulting in an oxidative addition reaction to form a π-allyl hydride intermediate.

The isomerization intermediate implicated is $HFe(CO)_3$(π-allyl) which can be formed by irradiation of $Fe(CO)_4$(alkene) or by thermal dissociation of an alkene from $Fe(CO)_3(alkene)_2$.[26]

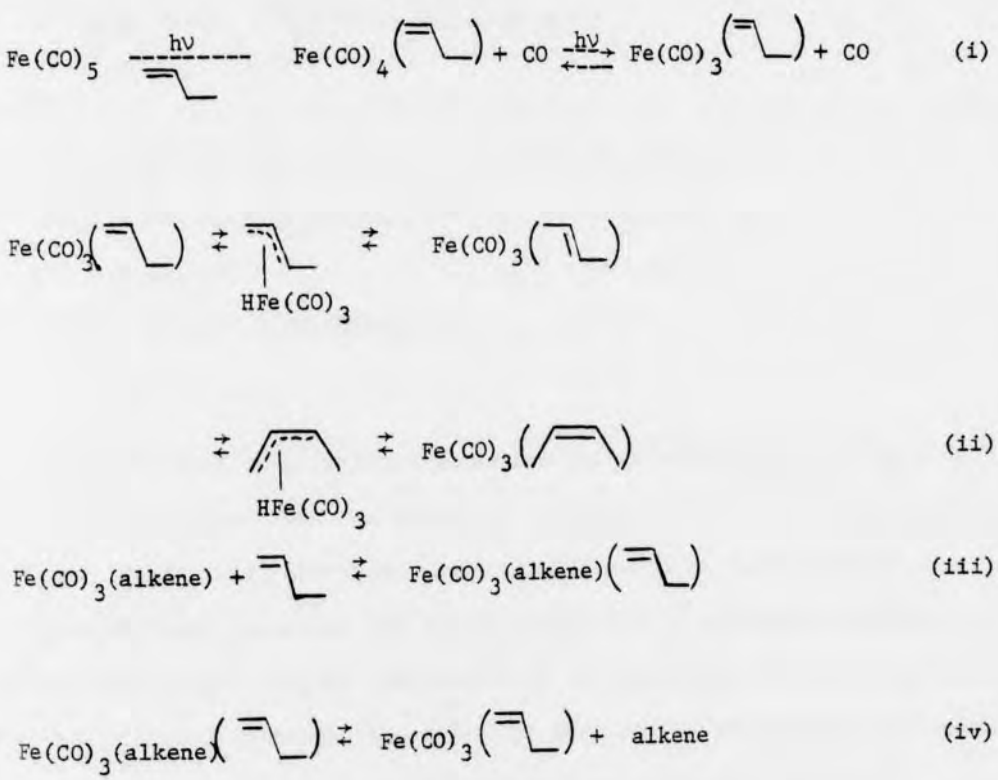
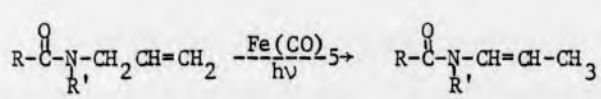


Figure 2

The $Fe(CO)_5$ induced isomerization of N-allylamides proceeds particularly cleanly in the presence of ultraviolet light. The process is useful in the preparation of N-2-propenyl amides, ureas, and carbamates since no side-products are formed. In some cases, problems of isolation decrease the actual yield. trans-Isomers are generally formed preferentially, at least during the early stages of the reaction.[28]

The mechanism proposed involves the intramolecular migration of an allylic proton via an unidentified intermediate coordination complex, probably similar to the π-complex detected in the case of allyl ethers.[28]



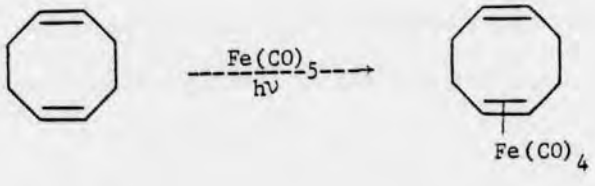
a) R = Me, R' = H
b) R = Me, R' = $CH_2CH=CH_2$
c) R = CF_3, R' = H
d) R = CF_3, R' = $CH_2CH=CH_2$
e) R = NH_2, R' = H
f) R = PhNH, R' = H
g) R = PhO, R' = H

The π-allyl metal hydride mechanism for rearrangements of the type just discussed has been the generally accepted mechanism for many years without substantial question. Other mechanisms have been proposed, but in general most proposals are modifications of the mechanism embodied in equation 2 (and 8) above. While most of the data thus far collected can be rationalized in terms of the π-allyl hydridoiron tricarbonyl mechanism, a significant number of results raise serious questions about the validity of the mechanism.

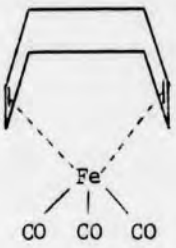
In the first instance much has been made of the fact that the thermodynamically most stable products predominate in rearrangements catalyzed by iron carbonyls. If the π-allyl complex were indeed a product controlling intermediate in these rearrangements, another result should be obtained, since it is well known that π-complexes of iron prefer to be less substituted where the opportunity exists.[7] The more highly substituted olefins are the compounds that are generally produced.

The work of Kerner von Gustorf[30] and Asinger[31] bring further doubt to the validity of the π-allyl mechanism. The work of the former investigator is here presented in some detail.

Illumination of 1,5-cyclooctadiene (40) and $Fe(CO)_5$ yielded an unstable oil identified as 1,5-cyclooctadieneiron tetracarbonyl (41), when one third of the $Fe(CO)_5$ was reacted. Its structure was supported by its oxidative degradation with $Ce(NH_4)_2(NO_3)_6$ in ethanol to 1,5-cyclooctadiene, as well as by spectroscopic evidence such as NMR, and infrared, and mass spectra, and by elemental analysis. However, extended irradiation yielded 1,5-cyclooctadieneiron tricarbonyl (42) as stable orange crystals. It was also found that the iron tetracarbonyl complex (41) on standing decomposed to 1,5-cyclooctadiene-bis(iron tetracarbonyl) (43) and yellow crystals which produced $Fe_3(CO)_{12}$ on slow heating above 77°C.



40 41



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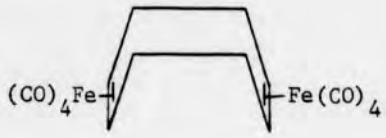


43

Of greatest importance in the work of Kerner von Gustorf, however, is the fact that none of the complexes 41, 42, or 43 yielded even traces of 1,3-cyclooctadiene or the complex 44. This tends to discredit the mechanisms already discussed. If the mechanisms were correct, 41 would be the intermediate for the production of the coordinatively unsaturated iron tricarbonyl complex (53, see page 31). This complex would extract a hydrogen from an allylic position to produce a π-allyl complex (54, see page 31) which would ultimately give rise to the complex 44. Some mechanistic pathway must be present which is significantly different from those already suggested.

1,3-Cyclooctadieneiron tricarbonyl (44) could be easily obtained in crystalline form from the photochemical reaction of $Fe(CO)_5$ and 1,3-cyclooctadiene. The 1,3-complex (44) seemed to be thermally less stable than the 1,5-complex (42) which may be due to conformational strain resulting when the conjugated double bonds are forced into one plane by coordination.[32]

44

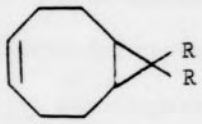
Our own results, like those of Kerner von Gustorf discussed above, also argue strongly against the operation of a π-allyl hydridoiron tricarbonyl mechanism. In the following section, our results will be presented and analyzed, and an alternative mechanism proposed to explain these results.

RESULTS AND DISCUSSION

In the previous section, a number of representative examples of olefinic rearrangement induced by iron carbonyls such as $Fe(CO)_5$ and $Fe_3(CO)_{12}$ was presented, and the generally accepted mechanism for these reactions, involving a π-allyl hydridoiron tricarbonyl intermediate, was discussed. Arguments were presented which appeared to support such a mechanism, and results which contradicted this explanation were discussed. These latter results, along with our own results obtained from systems which are about to be considered, have led us to the belief that there are certain systems for which the generally accepted mechanism may not be correct.

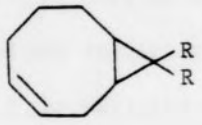
Our results, for the most part, were obtained from various bicyclo [6.1.0]nonenes shown in figure 3. We chose these particular olefins because, first of all, they possess a structural element which lends strain to the system, hence we expected them to undergo facile rearrangement when treated with various iron carbonyl reagents under a variety of conditions.[25,33] Secondly, they were readily synthesized using such methods as a modified Simmons-Smith[34] reaction and dichlorocarbene addition[35,36,37] to appropriate olefins.

The bicyclo[6.1.0]nonenes were synthesized by one general procedure. Bicyclo[6.1.0]non-4-ene (45) was prepared by reacting 1,5-cyclooctadiene under Simmons-Smith reaction conditions with zinc dust, copper(I) chloride, and methylene iodide. The yields were poor and purification of the product was difficult. The best method for purification was found to be



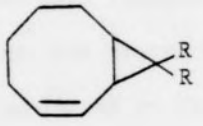
45. R = H bicyclo[6.1.0]non-4-ene

46. R = Cl 9,9-dichlorobicyclo[6.1.0]non-4-ene



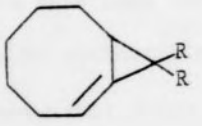
47. R = H bicyclo[6.1.0]non-3-ene

48. R = Cl 9,9-dichlorobicyclo[6.1.0]non-3-ene



49. R = H bicyclo[6.1.0]non-2-ene

50. R = Cl 9,9-dichlorobicyclo[6.1.0]non-2-ene



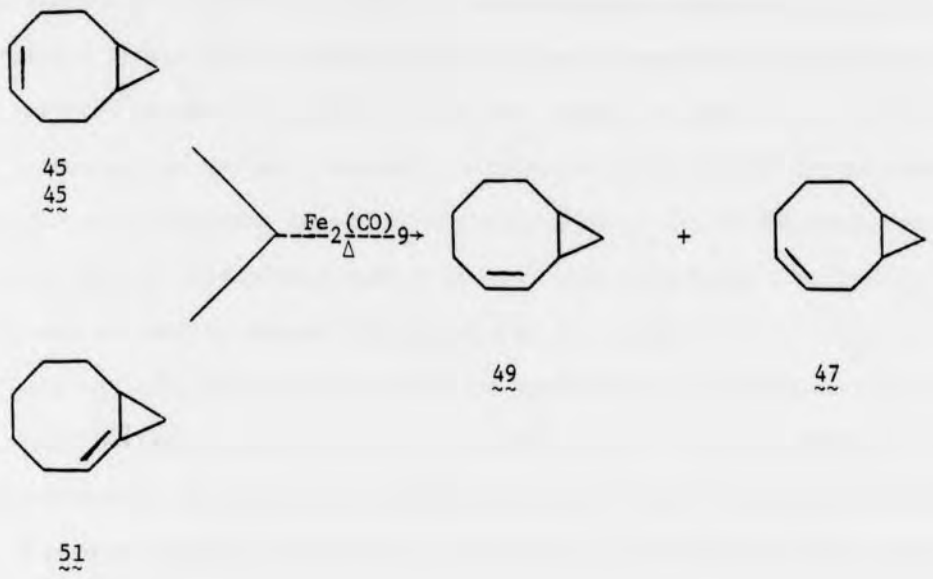
51. R = H bicyclo[6.1.0]n0n-1-ene

Figure 3

repeated distillation followed by chromatography on 5% silver nitrate-silica gel columns. This method provided product that was essentially pure. Bicyclo[6.1.0]non-2-ene (49) was prepared by a similar method, using 1,3-cyclooctadiene as the starting olefin. Bicyclo[6.1.0]non-1-ene (51) was prepared by reacting cyclooctene with potassium t-butoxide and bromoform which yielded 9,9-dibromobicyclo[6.1.0]nonane. The dibromide was treated with acetic acid and zinc dust to eliminate one of the bromides (presumably the exo-bromide), and the resulting 9-bromobicyclononane was treated with strong base to yield the ultimate product, bicyclo[6.1.0] non-1-ene (51).

Rearrangements of 4-ene (45) and 1-ene (51) were conducted in the following manner. The bicyclic olefin to be investigated was placed in hexane with a quantity of iron carbonyl (usually equimolar amounts of $Fe_2(CO)_9$), and the stirred mixture was heated to reflux under a nitrogen atmosphere. The reactions were monitored by the disappearance of the peak due to starting material in the gas-liquid chromatogram (GLC). Both 4-ene (45) and 1-ene (51) yielded a mixture of 2-ene (49) as the major product, and 3-ene (47). The GLC proved ineffective in analysis of these products, so that infrared spectra were used for identification by comparison with the infrared spectra of authentic samples.

From these results, it appeared that 2-ene (49) was the most thermodynamically stable of the bicyclic compounds. Were this the case, the bicyclic compound (49) should be unaffected by similar reaction conditions. However,when 2-ene (49) was placed in hexane with an equimolar amount of $Fe_2(CO)_9$ and the stirred mixture was heated to reflux under a nitrogen atmosphere no change was observed.

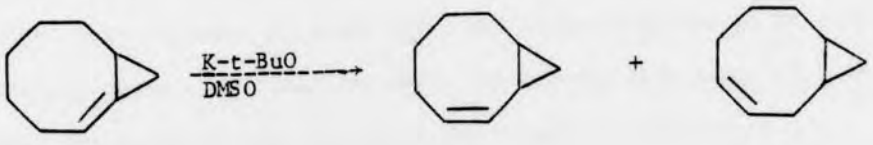


45
45

49 47

51

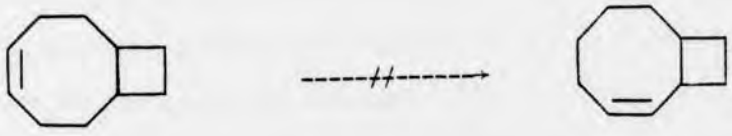
It is pertinent to this discussion to mention the results of Gardner et al regarding rearrangements of bicyclo[6.1.0]nonenes employing the potassium t-butoxide-dimethylsulfoxide system as the rearrangement medium.[35] In Gardner's investigation, 1-ene (51) was allowed to stand in the basic medium at room temperature for eighteen hours. At the end of the reaction time, the compound (51) was completely transformed to 2-ene (49) and 3-ene (47). The equilibrium composition of 2-ene (49) and 3-ene (47) was found to be 80:20, respectively, at 30°C.[35] However, the same composition was obtained from the base-catalyzed isomerization of 4-ene (45). These



51 49 47

results confirm our own beliefs that rearrangements catalyzed by iron carbonyls result in the production of the most thermodynamically stable uncomplexed product being formed. We were unable to detect the same ratio as accurately as Gardner reported, in spite of the fact that we employed columns and conditions described by Gardner, in as far as infrared spectra can be used in determining ratios, we were able to observe that 2-ene (49) was present in larger quantities than 3-ene (47).

Our initial suspicion was that the presence of the cyclopropyl group directly effected the course of the reaction, that is, the direction of rearrangement, by offering a complexation site to the iron carbonyl group. If this were correct, bicyclo[6.2.0]dec-4-ene (52) should not be subject to as rapid rearrangement, since cyclobutyl groups are known not to exhibit π-character to the extent that cyclopropyl groups do.[36] In fact, when 4-ene (52) was treated with $Fe_2(CO)_9$ under conditions similar to those which rearranged bicyclononenes such as 45, no reaction was observed.



52

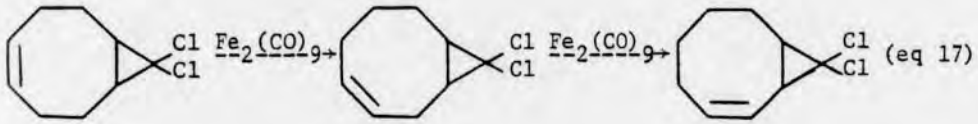
However, these results were not unambiguous; while iron carbonyls failed to effect rearrangement of 4-ene (52), the compound proved to be stable to strongly basic conditions, as well. It appears that 4-ene (52) is merely the most thermodynamically stable of the bicyclo[6.2.0]decenes.

Subsequently, X-ray data suggested that there was no interaction between the cyclopropyl moiety and the metal center, at least in certain related complexes in the solid state. These X-ray results will be discussed later.

A more efficient method for the formation of bicyclo[6.1.0]nonenes from cyclooctadienes was necessary in order to isolate the final product of rearrangement in higher yields and greater purity. The method found to be best was the addition of dichlorocarbene to an appropriate cyclooctadiene under phase-transfer conditions.[35,36,37] 9,9-Dichlorobicyclo [6.1.0]non-4-ene (46) was prepared from 1,5-cyclooctadiene in chloroform with aqueous sodium hydroxide and benzyltriethylammonium chloride, the phase-transfer reagent. The yields were good and purification was simple. 9,9-Dichlorobicyclo[6.1.0]non-2-ene (50) was prepared in the same manner, using 1,3-cyclooctadiene as the olefin acceptor of dichlorocarbene.

In reactions with iron carbonyls, 4-ene (46) was treated in a manner similar to that used previously for the corresponding hydrocarbon (45). The dichloride was placed in hexane with a quantity of $Fe_2(CO)_9$ and the stirred mixture was heated to reflux under a nitrogen atmosphere. The reaction was monitored by disappearence of the starting material peak on the GLC. The starting material 46 yielded a mixture of 2-ene (50) and 9,9-dichlorobicyclo[6.1.0]non-3-ene (48). As previously noted, the GLC was ineffective in distinguishing between the two products, so that infrared spectra were used for identification by comparison with the infrared spectra of authentic samples. The 2-ene (50) had unique peaks at 670, and 770 cm^{-1} whereas, peaks at 710, and 743cm^{-1} were used as positive identification of the 3-ene (48). In two separate experiments, it was

shown that 3-ene (48) was the source of 2-ene (50), i.e. 3-ene (48) was an intermediate in the rearrangement of 4-ene (46) to 2-ene (50). In the first experiment, the amount of 3-ene (48) was seen to diminish while 2-ene (50) was seen to increase with reaction time, and in the second, pure 9,9-dichlorobicyclo[6.1.0]non-3-ene (48) (prepared from 1,4-cyclooctadiene and chloroform by the phase-transfer method) produced 9,9-dichlorobicyclo[6.1.0]non-2-ene (50) when treated under identical reaction conditions.



(eq 17)

46 48 50

As discussed previously, the mechanism of iron carbonyl catalyzed rearrangement of olefins appears to us to be in doubt. Certain results, notably those of Kerner von Gustorf,[32] appear to contradict certain aspects of the π-allyl hydridoiron tricarbonyl mechanism (equations 2 and 8) usually accepted as the correct mechanism. It is well known that 1,5-cyclooctadiene (40) rearranges completely to 1,3-cyclooctadiene in the presence of $Fe(CO)_5$ at elevated temperature.[8] The π-allyl hydridoiron tricarbonyl mechanism requires initial formation of a monoolefiniron tetracarbonyl complex (41) as shown in the scheme below (Figure 4). Upon loss of carbon monoxide from the latter, the coordinatively unsaturated iron tricarbonyl species extracts a hydrogen atom from the host molecule

for stabilization to yield the π-allyl complex (54). However, Kerner von Gustorf and coworkers were able to isolate the monoolefiniron tetracarbonyl (41) by photochemical irradiation of 1,5-cyclooctadiene in the presence

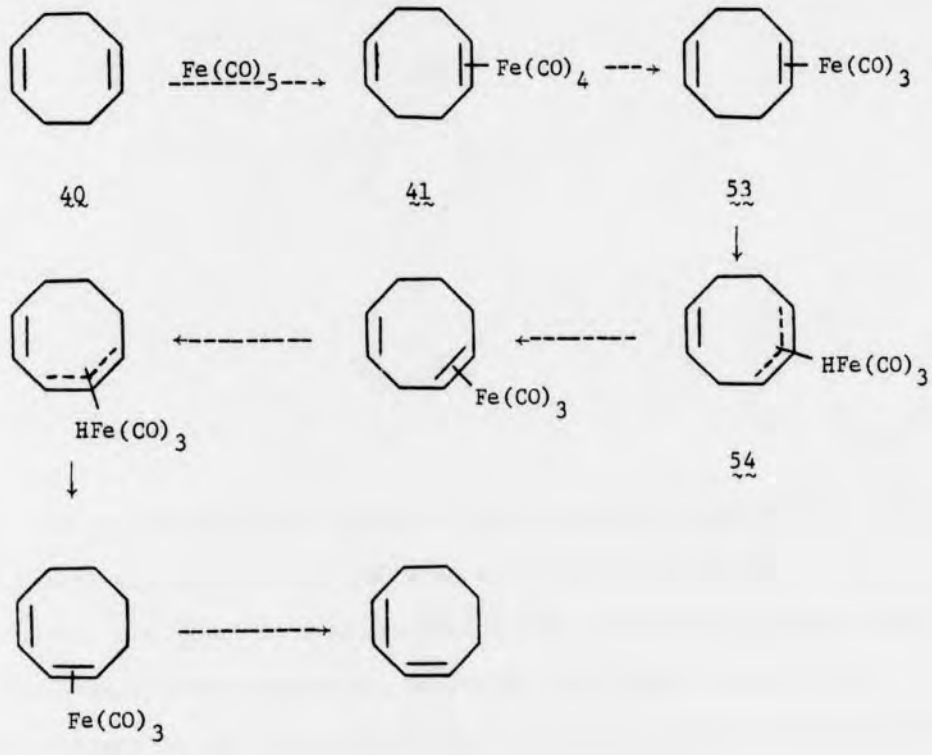
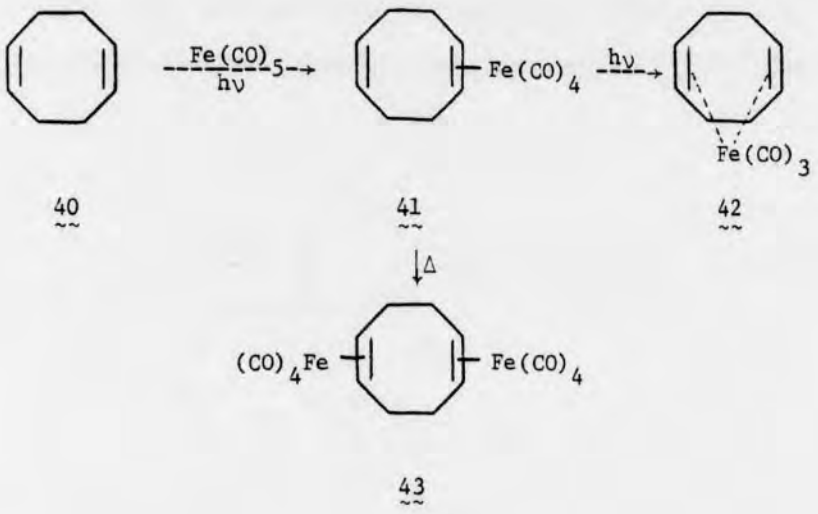


Figure 4

of $Fe(CO)_5$, and showed that its thermal activity was contrary to that required by the π-allyl hydridoiron tricarbonyl mechanism. Heating the tetracarbonyl complex 41 produced the bis(iron tetracarbonyl) complex 43 (Figure 5) and unrearranged 1,5-cyclooctadiene, and no 1,3-cyclooctadiene or the corresponding complex (44) were detected. These observations of course tend to shed doubt on the generally accepted mechanism.



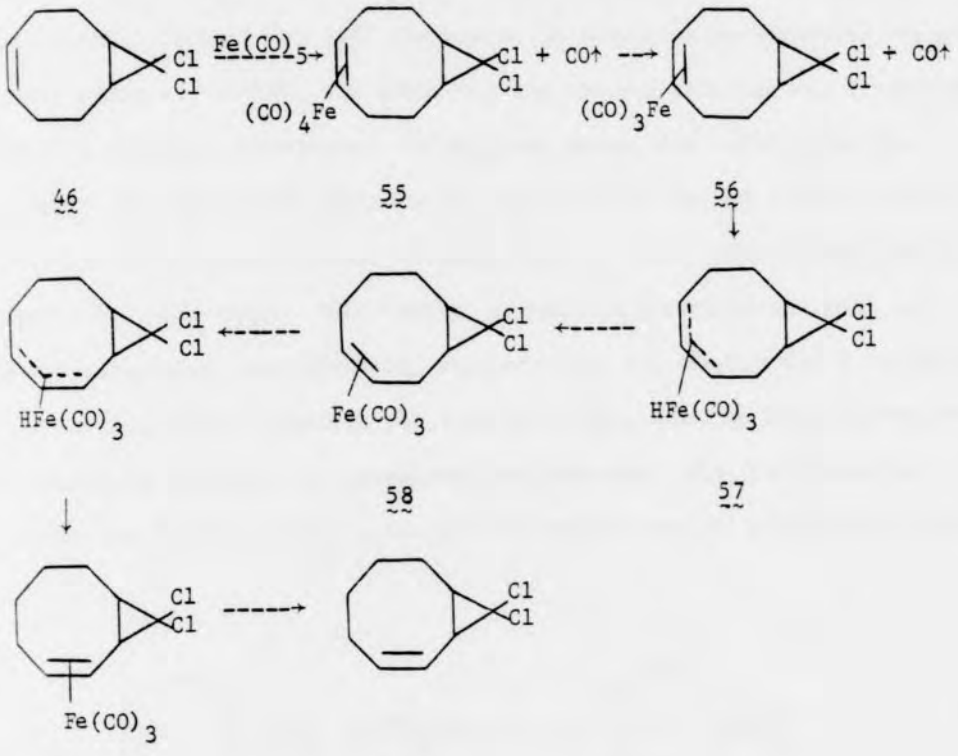
40 41 42

43

Figure 5

Our own results, like those of other workers discussed above, also argue strongly against the operation of a π-allyl hydridoiron tricarbonyl mechanism. In order to simplify discussion, let us first consider the π-allyl hydridoiron tricarbonyl mechansim as it might apply to the rearrangement of the 4-ene system (46). Were the mechansim operating in this case, the highly reactive $Fe(CO)_4$, produced by thermal degradation of $Fe_2(CO)_9$, would complex with the olefin, to produce the iron tetracarbonyl complex (55) (Figure 6). A molecule of carbon monoxide would be expelled to produce the coordinatively unsaturated complex (56), which because of its inherent instability would be converted to the π-allyl complex (57). The rearrangement would be complete after transfer of the hydrogen atom from the iron center in 57 to its new position on the host molecule, and subsequent decomplexation to yield the olefinic products.

The process could continue until the ultimate product, the most thermodynamically stable compound, in this case 2-ene (50), had been formed.

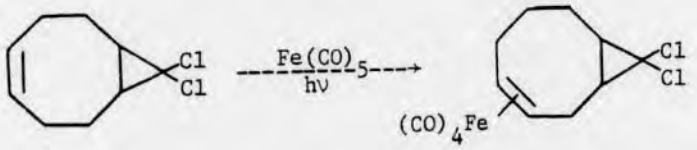


46 55 56 58 57 50

Figure 6

In order to determine the validity of the π-allyl hydridoiron tricarbonyl mechanism shown in figure 6, attempts were made to isolate the proposed complexes. Complexes could be detected in the metal carbonyl region of the infrared spectra of reaction mixtures obtained from

the $Fe_2(CO)_9$-bicyclo[6.1.0]nonene experiments, but isolation of these complexes was unsuccessful. An alternative route to these complexes would be photochemical synthesis, since such an approach was previously successful.[32] This was carried out in the following manner. 9,9-Dichlorobicyclo[6.1.0]non-4-ene (46) was placed in anhydrous deoxygenated reagent grade benzene. $Fe(CO)_5$ was added and the stirred solution was irradiated under a nitrogen atmosphere. After seven hours, the irradiation was stopped and the solvent evaporated. The residue yielded stable yellow platelet crystals which upon oxidative decomposition with $Ce(NH_4)_2(NO_3)_6$ left only 3-ene (48). This result, as well as elemental analysis and X-ray structural determination, suggests that the complex was 9,9-dichlorobicyclo[6.1.0]non-3-eneiron tetracarbonyl (59), arising from rearrangement of starting material and subsequent complexation. The X-ray results showed the $Fe(CO)_4$ group to be cis with respect to the cyclopropyl group,



(eq 18)

46 59

and because of the large distances involved, no evidence for interaction between the iron center and either the cyclopropyl group or the chlorine atoms could be found (Figure 7).[38]

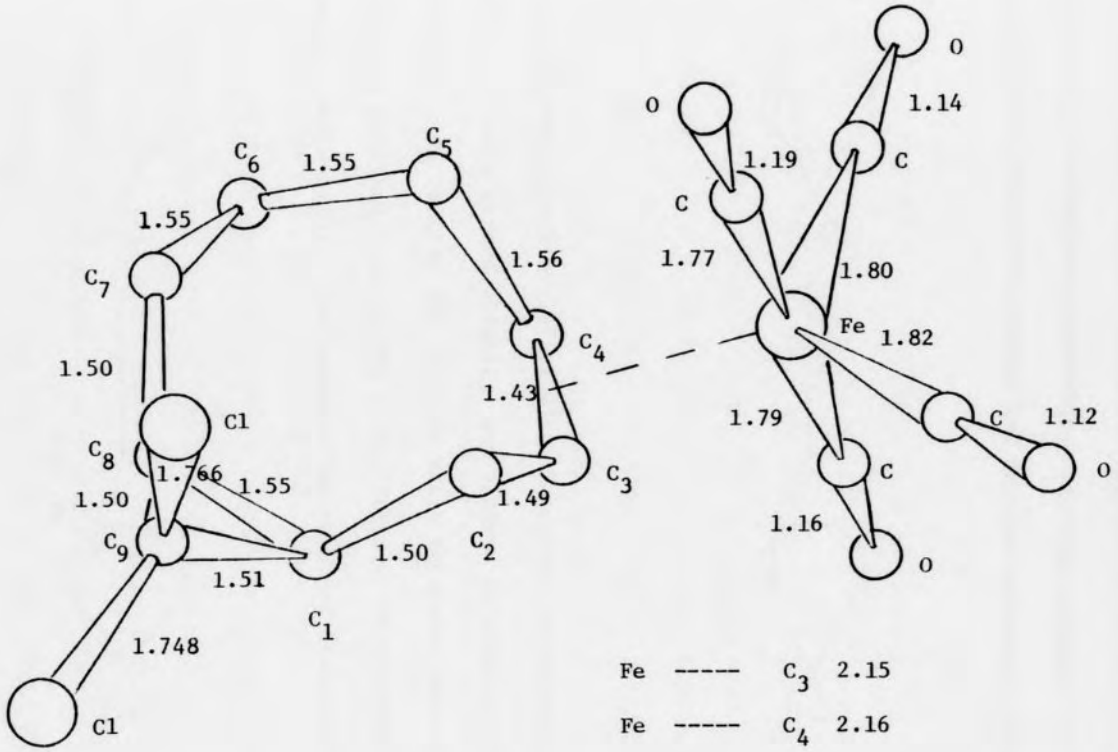
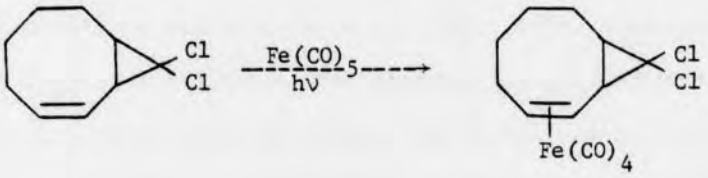

C6
1.55
C5
1.55
1.56
C7
C4
1.50
1.43
C1
C8
1.766
1.55
C3
1.50
1.49
C9
1.50
C2
1.51
C1
1.748
C1
O
O
1.14
1.19
C
C
1.77
1.80
Fe
1.82
1.79
C
1.12
C
O
1.16
O
Fe ----- C3 2.15
Fe ----- C4 2.16

Figure 7

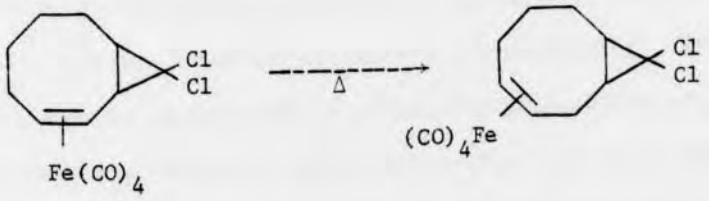
When 2-ene (50) was treated in a similar fashion with $Fe(CO)_5$ and ultraviolet irradiation, a complex was obtained which was crystalline, but thermally quite labile. Oxidative degradation of this complex with $Ce(NH_4)_2(NO_3)_6$ yielded the unrearranged starting material (50) as the only organic product, hence the complex was assigned structure 60 on this basis.



(eq 19)

50 60

When 9,9-dichlorobicyclo[6.1.0]non-2-eneiron tetracarbonyl (60) was placed in solvent, warmed slightly, and allowed to stand at room temperature, then cooled, the crystals which separated were not those of the starting material, but proved to be identical with those of the rearranged complex (59). Confirmation was obtained from oxidative



(eq 20)

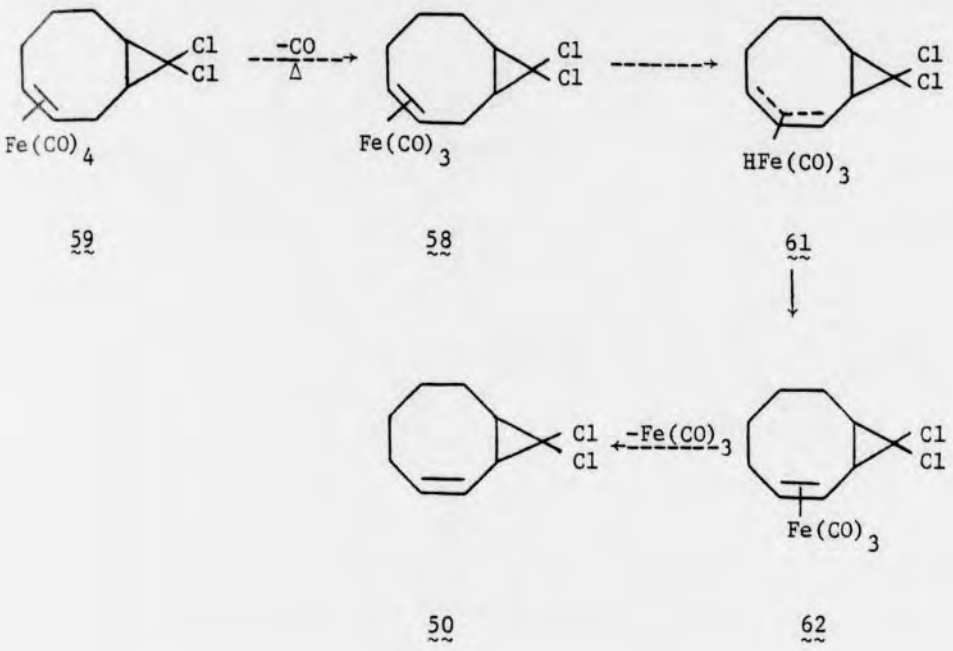
60 59

degradation of the new complex with $Ce(NH_4)_2(NO_3)_6$, which yielded only

3-ene (48). These results are of greatest importance in this project; not only do they show that the iron tetracarbonyl complex (59) is thermodynamically more stable than the iron tetracarbonyl complex (60), they also provide substantive evidence against the generally accepted π-allyl hydridoiron tricarbonyl mechansim. These aspects will be discussed momentarily.

To ascertain that an iron-containing species, such as $Fe(CO)_4$, was causing double-bond migration in 4-ene (46), rather than interaction of 46 with ultraviolet radiation, the compound was treated under conditions identical with those used previously, but in the absence of $Fe(CO)_5$. Thus, after seven hours of irradiation of 4-ene (46) in deoxygenated benzene solution under a nitrogen atmosphere, NMR analysis of the product showed only the presence of 46, hence confirming that an iron-containing species was responsible for reorganization in the bicyclo[6.1.0]nonene.

The body of evidence we have accumulated, as well as that of other investigators, especially Kerner von Gustorf and coworkers, leads us to the conclusion that the generally accepted mechansim is questionable. If this mechansim were correct as stated in figure 6, the iron tetracarbonyl complex (59) when heated would lose carbon monoxide to produce the unstable coordinatively unsaturated complex (58), which in turn would stabilize itself by formation of the π-allyl complex (61) (Figure 8). This species would be expected to ultimately produce the bicyclic compound (50) via the new tricarbonyl iron complex (62). In fact, however, we have shown that thermal decomposition of the monoolefiniron tetracarbonyl species (59), which we were able to isolate in pure form, gave no rearrangement product 50, and by implication could not have followed the mechanistic pathway indicated in figure 8.



59 58 61

50 62

Figure 8

Futhermore, rearrangement of a monoolefiniron tetracarbonyl complex can occur with the $Fe(CO)_4$ group intact. This observation argues strongly against the π-allyl hydridoiron tricarbonyl mechanism, since carbon monoxide in such a mechanism must be lost from the tetracarbonyl before rearrangement can proceed. We have seen, however, that the iron tetracarbonyl complex of 2-ene (50) rearranges in solution to complex 59, the iron tetracarbonyl complex of 3-ene (48). We have also observed this rearrangement during chromatography of 60 on alumina; the mechanism for rearrangement in this case, however, may not resemble that in solution. Figure 9 summerizes what we have said here.

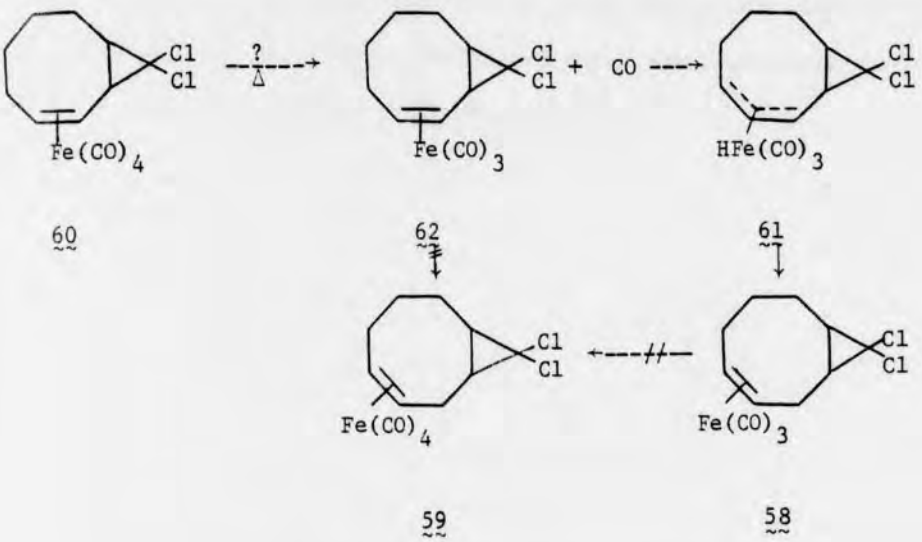
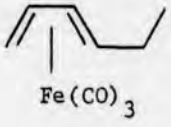


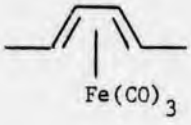
Figure 9

It appears that, at least for these bicyclo[6.1.0]nonenes and for 1,5-cyclooctadiene,[8,32] the π-allyl hydridoiron tricarbonyl mechanism cannot explain the observations. We have isolated iron tetracarbonyl complexes which are reluctant to rearrange (i.e. complex 59) or which rearrange with the $Fe(CO)_4$ group intact (i.e. complex 60). Furthermore, in nearly all cases studied in the entire area of iron carbonyl induced olefin rearrangement, the reactions have been observed to proceed in the direction of the most stable olefin. In cases where it is possible, rearrangement proceeds in the direction of the more substituted olefin (c.f. results of Casey and coworkers, ref. 20). This observation is contrary to the "desires" of an iron carbonyl reagent; in the normal case, where a complex is known to form, those complexes are more stable which are less heavily substituted, hence the 1,3-hexadieneiron tricarbonyl

complex (63) is more stable than that of the 2,4-hexadiene complex (64).[29] Nonetheless, were the π-allyl hydridoiron tricarbonyl mechanism correct, exactly the opposite effect would be operating.



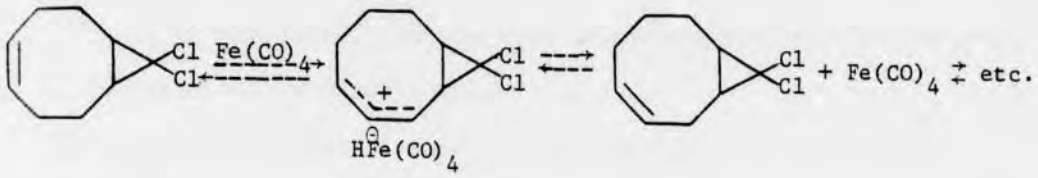
63



64

In the usual general case, iron carbonyl induced rearrangement proceeds in the same direction that would be expected in a rearrangement which proceeds via a cationic mechanism, i.e. an aluminum chloride catalyzed rearrangement. Using this fact as an indication of what may be taking place, we can offer an alternative mechanistic possibility to explain how iron carbonyls cause double bond shifts in olefins.

Instead of forming a complex with an olefin, which subsequently gives rise to a reactive intermediate in which hydrogen shift occurs (as in the π-allyl hydridoiron tricarbonyl mechanism), $Fe(CO)_4$, formed from $Fe(CO)_5$, $Fe_2(CO)_9$ or $Fe_3(CO)_{12}$ either thermally or photochemically, abstracts a hydride ion from the starting olefin to produce an ion pair (as in 65). Such an intermediate has two advantages over those of the π-allyl hydridoiron tricarbonyl mechanism. First of all, the $H\overset{\ominus}{Fe}(CO)_4$ anion is very stable[39] in the absence of air. Also, the cationic nature of the intermediate explains why these rearrangements appear to proceed in the direction in which cationic rearrangements proceed. The hydride ion in $H\overset{\oplus}{Fe}(CO)_4$



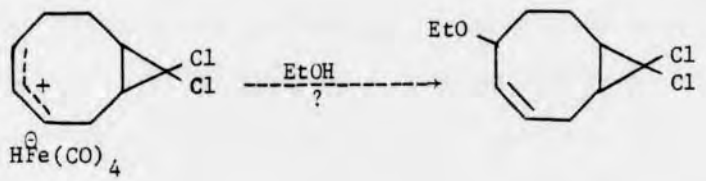
46 65

can be reincorporated into the hydrocarbon system either in its original position to reproduce starting material, or in a new allylic position to form a more stable olefin. The entire process can be repeated, ultimately giving rise to products. It is perhaps of substantial importance that when $Fe_2(CO)_9$ is used as the iron source, large amounts of $Fe_3(CO)_{12}$ are produced in the reaction mixture; $Fe_3(CO)_{12}$ can be thought to be a stable trimer of the $Fe(CO)_4$ species, which would be produced at the end of the reaction sequence.

At this stage of its development our mechanistic proposal is speculative, and lacks experimental proof. Two experiments which we have attempted to demonstrate the validity of this proposal have failed. The first was intended to determine the effect of solvent on the rate of rearrangement. If the transition state for the rate-determining step of the reaction is polar, as in 65 above, then polar solvents would stabilize the transition state and increase the rate of the reaction. When we conducted the reaction in tetrahydrofuran rather than hexane, otherwise under identical reaction conditions, we found that the reaction rate was

increased by an insignificant amount. If this mechanism is valid, then the formation of ion pairs such as 65 must occur in a non-rate-determining step. It is in fact likely that the rate determining step for the reaction is the formation of the $Fe(CO)_4$ species.

In another experiment, ethanol was used as solvent in anticipation that this nucleophile could compete with the anion in 65 for the cationic species. At best, we observed only traces of ethyl ethers such as 66. We chose to interpret this result as an inability of ethanol to compete favorably with the anion in 65, which is almost certainly very tightly held in an intimate ion pair arrangement. These two results are not



65 66

necessarily damaging to our mechanistic proposal. In fact, they are mutually consistent; since 65 appears not to be the transition state of a rate-determining reaction, one would expect its existence to be fleeting, hence it would not be likely that an external nucleophile such as ethanol could compete with the hydride ion in $H\overset{\ominus}{Fe}(CO)_4$.

The discussion which follows aims to demonstrate how our mechanistic proposal can be applied to olefin rearrangements catalyzed by iron

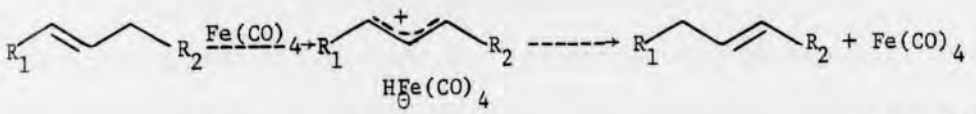
carbonyls in general. In Casey's work, isomerization of a mixture of 3-ethyl-1-pentene-3-d (24) in the presence of 3-methyl-1-butene (25) resulted in rearrangement products 26 and 27 in which deuterium remained exclusively in the ethylpentene skeleton (26), demonstrating that deuterium crossover had not occurred.

24 25 26 27

. Ford[24] obtained similar results. On heating the deuterio-alcohol (34) with $Fe(CO)_5$ in the presence of cyclohex-2-en-1-ol, only the deuterio ketone (35) and unlabelled cyclohexane were obtained, showing again that crossover of the deuterium had not occurred. These results, along with those of Casey,[20] suggest that the rearrangement occurs by intramolecular hydrogen transfer.

34 35

These observations can be explained nicely by invoking our cationic mechanism. There would be no deuterium exchange because of the tight ion pair formed between $H\overset{\ominus}{F}e(CO)_4$ and the cation, hence no deuterium exchange in Casey's work. In the case of Ford's observations, the deuterium can be placed in the exo-position without involving a π-allyl hydridoiron species because $D\overset{\ominus}{F}e(CO)_4$ is formed on the exo-side and for steric reasons cannot migrate to the endo-side. In general, it can be seen in equation 21 how our cationic mechanism is applied to other systems as well.



(eq 21)

In light of the present results, the π-allyl hydridoiron tricarbonyl mechanism has been shown to be unacceptable, and that the $H\overset{\ominus}{F}e(CO)_4$-cation mechanism is more reasonable. Problems with the π-allyl hydridoiron tricarbonyl mechanism have also been shown in the work of Kerner von Gustorf.[32] The monoolefiniron tricarbonyl complex (42) was isolated by photochemical irradiation of 1,5-cyclooctadiene in the presence of $Fe(CO)_5$. Heating the tetracarbonyl complex (41) produced the bis(iron tetracarbonyl) complex (43) and unrearranged 1,5-cyclooctadiene, and no 1,3-cyclooctadiene or the corresponding complex (44) was detected. This in itself tends to shed doubt on the generally accepted mechanism.

Our own results also argue strongly against the π-allyl hydridoiron tricarbonyl mechanism. The monoolefiniron tetracarbonyl complex,

9,9-dichlorobicyclo[6.1.0]non-3-eneiron tetracarbonyl (59) was isolated by photochemical irradiation of 9,9-dichlorobicyclo[6.1.0]non-4-ene (46) in the presence of $Fe(CO)_5$. When 9,9-dichlorobicyclo[6.1.0]non-2-ene (50) was treated in a similar fashion with $Fe(CO)_5$ and ultraviolet irradiation, 9,9-dichlorobicyclo[6.1.0]non-2-eneiron tetracarbonyl (60) was isolated. Futhermore, the monoolefiniron tetracarbonyl (60) was rearranged to the tetracarbonyl complex (59). This rearrangement occurred with the $Fe(CO)_4$ group intact. This sheds additional doubt on the generally accepted mec mechanism, since carbon monoxide in such a mechanism must be lost from the tetracarbonyl before rearrangement can proceed.

The evidence we have accumulated and presented in this thesis gives substantial support which argues strongly against the operation of a π-allyl hydridoiron tricarbonyl mechanism, while making the possibility of the $H\overset{\ominus}{F}e(CO)_4$-cationic mechanism more feasible.

EXPERIMENTAL

All NMR spectra were obtained with a Varian T-60 NMR spectrometer. Infrared spectra were obtained on a Perkin-Elmer 457 grating spectrometer using NaCl cells. Gas chromatographic analyses were performed on a Hewlett-Packard 5720A gas chromatograph. Melting points were obtained from a Fisher-Johns melting point apparatus; melting points and boiling points are uncorrected. Elemental analysis was obtained from Galbraith Laboratories, Inc., Knoxville, Tenn.. X-ray analysis was obtained from Dr. A. T. McPhail, Paul M. Gross Chemical Laboratory, Duke University, Durham, N. C..

General Procedure for the Preparation of Bicyclo[6.1.0]nonene.[34]

A mixture of zinc dust (8.0g, 0.123 mol) and cuprous chloride (1.2g, 0.123 mol) in 20 ml of anhydrous ether was stirred and heated to reflux in a nitrogen atmosphere for 30 min. Cyclooctadiene (5g, 0.046 mol) and methylene diiodide (16.3g, 0.061 mol) was thene added, and the mixture was maintained at reflux under a nitrogen atmosphere for 24 hr. The solution was cooled and filtered through Celite. The mixture was extracted twice with 30-ml portions of ether. The ethereal portion was washed with two 100-ml portions of saturated NH_4Cl, a 100-ml portion of saturated $NaHCO_3$, and 100 ml H_2O. The organic layer was dried over $MgSO_4$ and the solvent removed under reduced pressure. The yields were determined by gas chromatography since the compounds were difficult to separate from starting material by distillation.

Bicyclo[6.1.0]non-4-ene (45), from 1,5-cyclooctadiene: 35%, NMR (δ, neat) 5.6 (2H), 2.7-0.5 (11H), and -0.9 (1H); IR (thin film) 3065 (s), 2930 (s), 2865 (s), 1460 (m), 1016 (m), 850 (m), and 720 (s) cm^{-1}.

Bicyclo[6.1.0]non-2-ene (49), from 1,3-cyclooctadiene: 17%, NMR (δ, neat) 5.8-5.2 (2H), 2.7-0.5 (11H), and -0.9--0.7 (1H); IR (thin film) 3070 (m), 3000 (s), 2930 (s), 2860 (s), 1450 (s), 1026 (m), 764 (m), and 670 (m) cm^{-1}.

Bicyclo[6.1.0]nonane, from cyclooctene: 87%, IR (thin film) 3062 (w), 2990 (s), 2910 (s), 2855 (s), 1465 (m), 1446 (m), 1028 (m), 1004 (m), and 844 (m) cm^{-1}.

Rearrangement of Bicyclo[6.1.0]non-4-ene (45) with $Fe_2(CO)_9$.

The bicyclo[6.1.0] non-4-ene (45) (1g, 0.0082 mol) was dissolved in 5 ml of hexane and $Fe_2(CO)_9$ (1g, 0.0027 mol) was added. The system was flushed with nitrogen and maintained under a nitrogen atmosphere. The mixture was heated to reflux and stirred magnetically for 2 hr, then cooled, filtered through Celite filter-aid, and concentrated at reduced pressure. The residue was chromatographed on alumina using hexane as the eluent. The hexane was removed by distillation and the residue was distilled at reduced pressure, bp 80°(35-45mm). An infrared spectrum indicated the product to be mostly bicyclo[6.1.0]non-2-ene, by comparison with the infrared spectrum appearing in the literature.[35]

Preparation of Bicyclo[6.1.0]non-1-ene (51).[35]

To a solution prepared by dissolving 4.8g (0.122 mol) of potassium in 145 ml of dry t-butyl alcohol was added 12g (0.108 mol) cyclooctene. The solution was cooled in ice and 30.5g (0.120 mol) of bromoform was added dropwise with stirring. After the addition was complete, stirring

was continued for an hour and the contents were poured into 120 ml of water. The mixture was extracted several times with petroleum ether and the combined extracts were washed with water, dried over $MgSO_4$, and the solvent removed under reduced pressure. The residue was distilled under reduced pressure to yield 9,9-dibromobicyclo[6.1.0]nonane.

9,9-Dibromobicyclo[6.1.0]nonane (8.5g) was dissolved in 60 ml of glacial acetic acid and heated to 60°. The solution was stirred vigorously while 22.5g of zinc dust was added in small portions over a period of 2 hr and upon complete addition, the solution continued stirring for 30 hr at 60°. The mixture was filtered through Celite, poured into ice water and extracted with petroleum ether. The extracts were combined and washed with water. The organic layer was dried over $MgSO_4$, the solvent removed under reduced pressure, and the residue distilled to yield 5.0g of colorless endo-9-bromobicyclo[6.1.0]nonane.

To a solution prepared by dissolving potassium t-butoxide, made from 5g of potassium, in 200 ml of dry dimethylsulfoxide in a nitrogen atmosphere, was added 5.0g of endo-9-bromobicyclo[6.1.0]nonane. The solution was under nitrogen until a monitor sample indicated the disappearance of all starting material. The reaction was quenched in ice water and extracted with petroleum ether. The organic layers were combined, washed with water, dried over $MgSO_4$, and solvent removed under reduced pressure. The residue was flash distilled at reduced pressure and the distillate was redistilled to provide 3.5g of colorless bicyclo[6.1.0]non-1-ene, bp 83-85°(20mm), NMR (δ, neat) 5.8 (1H), 2.5-0.3 (13H), in agreement with physical and spectral properties obtained by Gardner et al.[35]

Rearrangement of Bicyclo[6.1.0]non-1-ene (51) with $Fe_2(CO)_9$.

Bicyclo[6.1.0]non-1-ene (51) (1g, 0.0082 mol) was dissolved in 5 ml of hexane and $Fe_2(CO)_9$ (1g, 0.0027 mol) was added. The system was flushed with nitrogen and maintained under a nitrogen atmosphere. The mixture was heated to reflux and stirred magnetically for 5 hr. At the end of the reaction time, the mixture was cooled, filtered through Celite, and concentrated. An infrared spectrum was obtained of the reaction mixture and it compared well with the infrared spectrum of bicyclo[6.1.0] non-2-ene, indicating that rearrangement was complete.

General Procedure for the Preparation of 9,9-Dichlorobicyclo[6.1.0]nonenes.[37]

A mixture of 54g of cyclooctadiene and 65g of chloroform was cooled to 10°. The solution was stirred vigorously while 100 ml of 50% sodium hydroxide solution was added. The mixture was again cooled to 10° and 1.5g of the phase-transfer reagent, benzyltriethylammonium chloride, was added. The temperature gradually rose and was maintained at about 42° with an ice-water bath. Once the temperature began to drop, the bath was removed but the temperature was carefully monitored. The mixture was stirred vigorously for an additional 2 hr. The reaction mixture was poured into water and extracted with ether. The ethereal layers were combined, washed with water, and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue distilled.

9,9-Dichlorobicyclo[6.1.0]non-4-ene (46), from 1,5-cyclooctadiene: 40.7g, 43% ($110-113^{\circ}$/13mm), IR (thin film) 3018, 2940, 2890, 1482, 1445, 1435, 1205, 1175, 1104, 1014, 964, 826, 779, and 715 cm^{-1}.

9,9-Dichlorobicyclo[6.1.0]non-2-ene (50), from 1,3-cyclooctadiene: 53.1-55.6g, 72-75% ($106-110^{\circ}$/10mm), IR (thin film) 3025, 3005, 2930, 2860, 1455, 1223, 1176, 1090, 830, 814, 775, 770, 741, and 671 cm^{-1}.

9,9-Dichlorobicyclo[6.1.0]non-3-ene (48), from 1,4-cyclooctadiene: IR (thin film) 3020, 2935, 2862, 1460, 1444, 1175, 1100, 1030, 889, 860, 834, 810, 744, 710, and 670 cm^{-1}.

Preparation of 1,4-Cyclooctadiene.[39]

To 105.4g of freshly distilled 1,3-cyclooctadiene in 400 ml of carbon tetrachloride was added 175g of NBS and 1.25g of benzoyl peroxide. The mixture was refluxed, with stirring, for 17 hr, then cooled and the succinimide removed by filtration. The filtrate was washed with two 600-ml portions of 10% $NaHCO_3$ and 600 ml H_2O and then dried over $MgSO_4$. The solvent was removed under reduced pressure (20mm) through a Vigreux column. The residue was distilled through a short-path distillation column to give 91.5g of a bromide mixture, bp 25-52°(0.3mm).

To a suspension of 15g of lithium aluminum hydride in 250 ml of anhydrous ether was added, dropwise and with stirring, 97.1g of the bromide mixture in 25 ml of ether. Following complete addition, the solution was refluxed overnight. After cooling, 40 ml of H_2O was cautiously added, dropwise and with stirring, to the externally cooled solution. Sulfuric acid (20%, 100 ml) was then added in a similar manner, followed by 400 ml more of the acid added at room temperature. Stirring was continued until al of the white precipitate, formed on H_2O addition, had dissolved. The aqueous portion was separated and extracted with 250 ml of ether. The latter was added to the original organic layer and the combined extracts were washed with two 400-ml portions of 10% $NaHCO_3$ and 400 ml of H_2O, and dried over $MgSO_4$. The ether was removed by distillation leaving 50.5g of diene mixture.

To 50.5g of the diene mixture was added 140 ml of 50% aqueous $AgNO_3$. The mixture was stirred, in the dark, overnight. The silver nitrate complex, a green solid, was isolated by filtration and washed with several portions of ether which were then added to the filtrate. The complex was further washed with acetone and again with ether and then dried. The filtrate was separated into aqueous and organic portions and the latter reextracted with 100-, 75-, and 75-ml portions of 50% $AgNO_3$. The remaining organic layer, after washing with H_2O, drying over $MgSO_4$, and concentration, gave 22.5g of 1,3-cyclooctadiene. Each aqueous $AgNO_3$ extract, including that from the original filtrate, was washed with ether to remove any residual 1,3-cyclooctadiene. To the combined ether-washed $AgNO_3$ extracts was added, with external cooling and stirring, 250 ml of cold, concentrated NH_4OH. After stirring for 15 min, the resultant mixture was extracted with two 500-ml portions of ether. Similarly, the dried solid complex was dissolved in 350 ml of cold, concentrated NH_4OH (a small amount of greyish residue remained insoluble) and carefully extracted with two 300-ml portions of ether. The ether extracts from the solid complex and the aqueous $AgNO_3$ portions were combined, washed with water, dried over $MgSO_4$, and concentrated by distillation. The residue was further distilled through a microdistillation column to give 13.3g of 1,4-cyclooctadiene, bp 57-58°(35mm).

Rearrangement of 9,9-Dichlorobicyclo[6.1.0]non-4-ene (46) with $Fe_2(CO)_9$.

9,9-Dichlorobicyclo[6.1.0]non-4-ene (46) (1g, 0.0052 mol) was dissolved in hexane and $Fe_2(CO)_9$ (1g, 0.0027 mol) was added. The system was flushed with nitrogen and maintained under a nitrogen atmosphere. The mixture was heated to reflux and stirred magnetically for 2 hr, then

cooled, filtered through Celite filter-aid, and concentrated at reduced pressure. The residue was chromatographed on alumina using hexane as the eluent. The hexane was removed under reduced pressure, and the residue distilled, bp 96°/7.5mm. An infrared spectrum indicated that the product was mostly 9,9-dichlorobicyclo[6.1.0]non-2-ene (50) with smaller amounts of 9,9-dichlorobicyclo[6.1.0]non-3-ene (48).

Preparation of 9,9-Dichlorobicyclo[6.1.0]non-3-eneiron Tetracarbonyl (59).

A solution of 10g (0.052 mol) of 9,9-dichlorobicyclo[6.1.0]non-4-ene in 545 ml of anhydrous reagent grade benzene was placed in an irradiation vessel. Nitrogen was bubbled through the solution for 15-20 min to deoxygenate the solution. A quartz cold finger containing a 450 watt Hanovia medium pressure lamp and a Pyrex filter was inserted into the vessel. The system was maintained under a nitrogen atomsphere and 10g of $Fe(CO)_5$ was added. The mixture was irradiated and stirred magnetically for 7 hr with periodic removal of $Fe_2(CO)_9$ from the cold finger. The mixture was filtered and the benzene was removed at reduced pressure while maintaining the temperature below 35°. The residue was cooled to -5°, with separation of a yellow crystalline material. The crystals were collected by filtration and recrystallized from acetone to yield yellow platelets, mp 84.5-85.5° (dec).

Anal. Calcd. for $C_9H_{12}Cl_2 \cdot Fe(CO)_4$: %C 43.55; %H 3.65; %Cl 21.42. Found: %C 43.59; %H 3.51; %Cl 19.64.

The yellow platelets (0.5g) were dissolved in acetone and $Ce(NH_4)_2(NO_3)_6$ was added slowly with stirring. Evolution of CO was observed and addition was stopped when gas evolution ceased. The solution was poured into water and the aqueous solution was extracted several times with petroleum ether.

The organic solutions were combined, washed with water, and dried over $MgSO_4$. The solvent was removed under reduced pressure. An infrared spectrum was obtained of the residue and showed it to be exclusively 9,9-dichlorobicyclo[6.1.0]non-3-ene, indicating that the complex had been of the 9,9-dichlorobicyclo[6.1.0]non-3-ene (48).

Preparation of 9,9-Dichlorobicyclo[6.1.0]non-2-eneiron Tetracarbonyl (60).

The procedure followed that which was described above for the preparation of 9,9-dichlorobicyclo[6.1.0]non-3-eneiron tetracarbonyl.

After removing the benzene, the residue yielded yellow needle-like crystals, mp 75-77° (dec). The yellow needles (0.5g) were dissolved in acetone and $Ce(NH_4)_2(NO_3)_6$ was added slowly with stirring. Evolution of CO was observed and addition was stopped when gas evolution ceased. The solution was poured into water and the aqueous solution was extracted several times with petroleum ether. The organic layers were combined, washed with water, and dried over $MgSO_4$. The solvent was removed under reduced pressure. An infrared spectrum was obtained and showed it to be exclusively 9,9-dichlorobicyclo[6.1.0]non-2-ene, indicating that the complex had been that of the 9,9-dichlorobicyclo[6.1.0]non-2-ene (50).

Rearrangement of 9,9-Dichlorobicyclo[6.1.0]non-2-eneiron Tetracarbonyl (60) to 9,9-Dichlorobicyclo[6.1.0]non-3-eneiron Tetracarbonyl (59).

9,9-Dichlorobicyclo[6.1.0]non-2-eneiron tetracarbonyl (60) was dissolved in acetone at 30-35°. The solution was cooled to -5°, with separation of a yellow crystalline material. The crystals obtained were yellow platelets, mp 84-85° (dec). After comparison of infrared spectra, the crystals were found to be 9,9-dichlorobicyclo[6.1.0]non-3-eneiron tetarcarbonyl (59).

The same results were obtained when 9,9-dichlorobicyclo[6.1.0]non-2-eneiron tetracarbonyl (60) was dissolved in hexane and chromatographed on alumina using hexane as the eluent. The hexane was removed under reduced pressure and the residue was filtered. The solid was dissolved in hexane and cooled to -5°, with separation of a yellow crystalline material. The crystals were collected by filtration to yield yellow platelets, 86-87°. Again, comparison of infrared spectra indicated the crystals to be 9,9-dichlorobicyclo[6.1.0]non-3-eneiron tetracarbonyl (59).

REFERENCES

1. For reviews of transition metal catalysis of olefin isomerization, see a) N. R. Davies, Rev. Pure Appl. Chem., 17, 83 (1967); b) C. W. Bird, "Transition Metal Intermediates in Organic Synthesis," Academic Press, New York, N. Y., 1967, p 67; c) M. Orchin, Adv. Catal. Relat. Subj., 16, 1 (1966); C. A. Tolman in "Transition Metal Hydrides," Vol. 1, E. L. Muetterties, Ed., Marcel Dekker, New York, N. Y., 1971, Chapter 6.
2. N. R. Davies, Aust. J. Chem., 17, 212 (1964).
3. G. I. Karapinka and M. Orchin, J. Org. Chem., 26, 4187 (1961); R. W. Goetz and M. Orchin, J. Am. Chem. Soc., 85, 1549 (1963); P. Taylor and M. Orchin, ibid, 93, 6504 (1971); and B. Fell, P. Krings and F. Asinger, Chem. Ber., 99, 3688 (1966).
4. R. Cramer, J. Am. Chem. Soc., 88, 2272 (1966); R. Cramer and R. V. Lindsey, Jr., ibid, 88, 3534 (1966); and C. A. Tolman, ibid, 94, 2994 (1972).
5. R. W. Adams, G. E. Batley, and J. C. Bailar, Jr., ibid, 90, 6051 (1968).
6. A. J. Deeming, S. S. Ullah, A. J. P. Domingos, B. F. G. Johnson, and J. Lewis, J. C. S., Dalton, 2093 (1974).
7. R. Pettit and G. F. Emerson, Adv. Organometal. Chem., 1, 1 (1964).
8. J. E. Arnet and R. Pettit, J. Am. Chem. Soc., 83, 2954 (1961).
9. F. Asinger and O. Berg, Chem. Ber., 88, 445 (1955).
10. G. F. Emerson and R. Pettit, J. Am. Chem. Soc., 84, 4591 (1962).

11. R. Damico and T. J. Logan, J. Org. Chem., 32, 2356 (1967).

12. F. Asinger, B. Fell, and G. Collin, Chem. Ber., 96, 716 (1963).

13. T. A. Manual, J. Org. Chem., 27, 3941 (1962).

14. F. Asinger, B. Fell, and K. Schrage, Chem. Ber., 98, 381 (1965).

15. R. Damico, J. Org. Chem., 33, 1550 (1968).

16. A. J. Hubert, Chem. and Ind., 975 (1968).

17. G. J. Meiszwolf, J. A. A. Van Drunnen, and M. Kloosterziel, Rev. Trav. Chim., 88, 1377 (1969); M. Kloosterziel and J. A. A. Van Drunnen, ibid, 89, 37 (1970); and S. Bank, A. Schriesheim, and C. A. Rowe, J. Am. Chem. Soc., 87, 3244 (1965).

18. T. J. Prosser, J. Am. Chem. Soc., 83, 1701 (1961); C. S. Price and W. H. Snyder, Tet. Letters, 69 (1962); and P. Canbere and M. F. Hocher, Bull. Soc. Chim. France, 459 (1968).

19. A. J. Hubert, A. Georis, R. Warin and P. Teyssie', J. C. S., Perkin II, 366 (1972).

20. C. P. Casey and C. R. Cyr, J. Am. Chem. Soc., 95, 2248 (1973).

21. R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, 1970.

22. F. G. Cowherd and J. L. von Rosenberg, J. Am. Chem. Soc., 91, 2157 (1969).

23. W. T. hendrix, F. G. Cowherd and J. L. von Rosenberg, J. Chem. Soc. (D), 97 (1968).

24. J. U. Strauss and P. W. Ford, Tet. Letters, 2917 (1975).

25. K. Cann and J. C. Barborak, J. Chem. Soc., Chem. Comm., 190 (1975).

26. M. A. Schroeder and M. S. Wrighton, J. Am. Chem. Soc., 98, 551 (1976).

27. F. W. Grevels, D. Schulz and E. Kerner von Gustorf, Angew. Chem., Int. Ed. Engl., 13, 534 (1974).

28. A. J. Hubert, P. Moniotte, G. Goebbels, R. Warin and P. Teyssie', J. C. S., Perkin II, 1954 (1973).

29. G. F. Emerson and R. Pettit, unpublished results.

30. E. Kerner von Gustorf, M. C. Henry and D. J. McAdoo, Liebigs Ann. Chem., 707, 190 (1967).

31. F. Asinger, B. Fell and K. Schrage, Chem. Ber., 98, 372 (1965).

32. E. Kerner von Gustorf and J. C. Hogan, Tet. Letters, 3191 (1968).

33. K. Cann, Masters Thesis, University of North Carolina at Greensboro, N. C., 1975; and J. C. Barborak, M. Russ, C. Manly, and E. Smith, unpublished results.

34. R. J. Rawson and I. T. Harrison, J. Org. Chem., 35, 2057 (1970).

35. C. L. Osborn, T. C. Shields, B. A. Shoulders, J. F. Krause, H. V. Cortez and P. D. Gardner, J. Am. Chem. Soc., 87, 3158 (1965).

36. C. A. Coulson and T. H. Goodwin, J. Chem. Soc., 2851 (1962); C. A. Coulson and T. H. Goodwin, J. Chem. Soc., 3161 (1963); D. Peters, Tetrahedron, 1539 (1963); R. Hoffmann and R. B. Davidson, J. Am. Chem. Soc., 93, 5699 (1971).

37. J. C. Barborak, unpublished results.

38. A. T. McPhail and K. D. Onan, unpublished results.

39. J. C. Barborak, J. Nichols, and L. James, unpublished results.

40. S. Moon and C. R. Ganz, J. Org. Chem., 34, 465 (1969).